

**HYDROPHILIC INDEX FOR AQUEOUS, LIQUID LAUNDRY DETERGENT
COMPOSITIONS CONTAINING LAS**

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TECHNICAL FIELD

The present invention relates to stable, aqueous heavy duty liquid laundry detergent compositions comprising linear alkyl benzene sulfonate and other surfactants, and fatty acids. The surfactant system is selected by calculating an optimal Hydrophilic Index, which results in 15 detergent compositions that provide superior cleaning benefits.

BACKGROUND OF THE INVENTION

The art is replete with examples of laundry detergent compositions that have good cleaning properties. Although many of these are liquids, the formulation of liquid detergent compositions 20 present numerous problems to the formulator, including how to optimize the surfactant system to achieve optimal cleaning.

Attempts to formulate liquid laundry detergent compositions in the past have included the use of various surfactants and combinations of surfactants. Formulators have typically relied on experimental methods for determining the optimal surfactant system. The procedure of 25 formulating various detergent compositions and testing the results is labor intensive, expensive and inexact. This problem is compounded by the large number of different surfactants that are available to detergent formulators.

Therefore, there is a continuing need for reliable and inexpensive methods to formulate an optimal surfactant system for use in a heavy duty liquid laundry detergent composition. The 30 method should relieve the formulator of excessive experimentation with various surfactant combinations. Moreover, the method should result in a surfactant system that provides superior cleaning benefits. The method should work for both structured and unstructured aqueous, heavy duty liquid detergent compositions. The compositions and methods of this invention meet these needs.

SUMMARY OF THE INVENTION

The present invention encompasses a heavy duty liquid laundry detergent compositions comprising a surfactant system, wherein the surfactant system comprises from about 0.1% to 5 about 20%, preferably from about 0.5% to about 19%, and more preferably from about 1% to about 18%, by weight of the surfactant system of an alkyl benzene sulfonate surfactant. The surfactant system has a Hydrophilic Index, HI_C , of from about 8.0 to about 9.2, preferably from about 8.2 to about 9.1, and more preferably from about 8.4 to about 9.0. The Hydrophilic Index can be calculated as follows:

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$$HI_C = \sum_y (\text{weight \% of surfactant } y \text{ in the surfactant system}) \times (HI_{Sy}).$$

HI_{Sy} is calculated for each of the surfactants in the surfactant system as follows:

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$$HI_{Sy} = 20 \times (\text{the molecular weight of the hydrophilic portion of surfactant component } y) / (\text{the molecular weight of surfactant component } y).$$

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Preferably the surfactant system comprises surfactants selected from the group consisting of non-soap anionic, nonionic, cationic, amphoteric, amine, poly hydroxy fatty acid amines and mixtures thereof, and the detergent composition preferably comprises no additional surfactants beyond those in the surfactant system. The surfactant system should comprise from 10% to about 40%, preferably from about 12% to about 35%, and most preferably from about 15% to about 32%, by weight of the composition.

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The compositions of the present invention also preferably comprise specific enzymes and fatty acids. Specifically, the present heavy duty liquid laundry detergent compositions preferably comprise a detergents amount of an enzyme selected from the group consisting of alkaline protease, mannanase, α -amylase variants, and mixtures thereof, preferably the enzyme is present in an amount of from about 0.0001% to about 1.5%, more preferably from about 0.00018% to about 1.0%, and most preferably from about 0.00024% to about 0.5%, by weight of the detergent composition of the pure enzyme. And the present compositions preferably further comprise from about 5% to about 20% by weight of the composition of a fatty acid.

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In addition to the essential surfactant system and the preferred enzymes and fatty acids, the detergent compositions of this invention preferably additionally comprise adjunct ingredients selected from the group consisting of non-citrate builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, additional enzymes, suds

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suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, antiredeposition agents, antifading agent, chelants, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

It has now been unexpectedly found that aqueous, heavy duty liquid detergent compositions containing a surfactants system, which comprises linear alkyl benzene sulfonate in a specific range and has a Hydrophilic Index in a specific range, have superior cleaning benefits when compared to compositions having a Hydrophilic Index or linear alkyl benzene sulfonate outside the ranges claimed herein. Moreover, the Hydrophilic Index provides an inexpensive, quick and reliable method for formulators to optimize a surfactant system that contains linear alkyl benzene sulfonate and at least one other surfactant. The compositions and methods defined herein are applicable to both structured and unstructured aqueous, heavy duty liquid detergent compositions.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}\text{C}$) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has now been found that a stable, aqueous heavy duty liquid detergent composition is surprisingly formed when a surfactant system is used that comprises linear alkyl benzene sulfonate in a specific percentage of the overall surfactant system. The surfactant system should be selected to be within the Hydrophilic Index of the present claims. While the Hydrophilic Index is defined above, and exemplified in the Example section below, a more thorough background may be helpful for the formulator.

It is well known that surfactant molecules have a hydrophilic portion (sometimes referred to as the "head") and a hydrophobic portion (sometimes referred to as the "tail"). The Hydrophilic Index of the present invention is determined from the percent, by weight, of each surfactant that is hydrophilic. Those skilled in the art of detergent formulation will know which portions of a surfactant molecule are hydrophilic and which are hydrophobic. And examples of how to calculate this Index for some of the most common surfactants are given in Example I below.

The Hydrophilic Index for a surfactant molecule is referred to herein as HI_S . The Hydrophilic Index for any given surfactant system can be summing the weight averaged HI_S for each surfactant in the surfactant system. The weight averaged HI_S can be calculated by multiplying the HI_S of each surfactant in the system by the weight percent of the surfactant

relative to the surfactant system. The Hydrophilic Index for a surfactant system is referred to herein as HI_C . Examples of the HI_C calculation for compositions according to the present invention, and for comparative compositions outside of the present claims, can be found in Example II below.

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Anionic Surfactants

The surfactant systems of the present invention comprise linear alkyl benzene sulphonates and may also comprise other anionic surfactants such as, alkyl sulfates, alkyl polyethoxylate sulfates and mixtures thereof. The detergent compositions of the present invention may contain other non-soap anionic surfactants.

Generally speaking, anionic surfactants useful herein are disclosed in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent No. 3,919,678, Laughlin et al, issued December 30, 1975, both incorporated herein by reference.

Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylolammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil.

Other anionic surfactants herein are the water-soluble salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water-soluble salts of esters of a-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and b-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

The alkyl polyethoxylate sulfates useful herein are of the formula

$$\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3^-\text{M}^+$$

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wherein R is an alkyl chain having from about 10 to about 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 0.5 to about 15.

Preferred alkyl sulfate surfactants are the non-ethoxylated C₁₂-15 primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than about 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates.

Nonionic Surfactants

Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, 10 Laughlin et al., issued December 30, 1975, and U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981. Exemplary, non-limiting classes of useful nonionic surfactants include: C₈-C₁₈ alkyl ethoxylates ("AE"), with EO about 1-22, including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propanoxy), alkyl dialkyl amine oxide, alkanoyl glucose amide, and mixtures thereof.

If nonionic surfactants are used, the compositions of the present invention will preferably contain up to about 10%, preferably from 0% to about 5%, more preferably from 0% to about 3%, by weight of a nonionic surfactant. Preferred are the ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC₂H₄)_nOH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in 20 U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981. Particularly preferred are ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of ethoxylation of from about 6 to about 12 moles of ethylene oxide per 25 mole of alcohol.

Other nonionic surfactants for use herein include:

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 30 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

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These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched,

5 primary or secondary, and generally contains from about 8 to about 22 carbon atoms.

Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type

include Tergitol® 15-S-9 (the condensation product of C₁₁-C₁₅ linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary

10 alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), Neodol® 23-6.5 (the condensation product of C₁₂-C₁₃ linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of

15 C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of C₁₄-C₁₅ linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic

15 surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl

ethoxylates."

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits

25 water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic® surfactants, marketed by BASF.

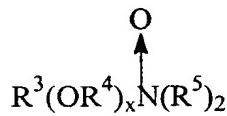
The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with

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ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic® compounds, marketed by BASF.

5 Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected
10 from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

15 Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R³ is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

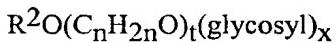
These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

25 Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or
30 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The

intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

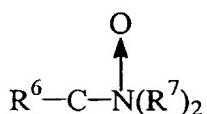
Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyl, decyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexa-glucosides.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:



wherein R^6 is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each R^7 is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and -(C²H₄O)_xH where x varies from about 1 to about 3.

Preferred amides are C₈-C₂₀ ammonia amides, monoethanolamides, dietha-nolamides, and isopropanolamides.

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Cationic and Amphoteric Surfactants

Non-quaternary, cationic detergents can also be included in detergent compositions of the present invention. Cationic surfactants useful herein are described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

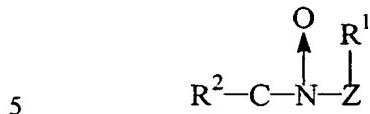
- 5 Ampholytic surfactants can be incorporated into the detergent compositions hereof. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an
10 anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Preferred amphoteric include C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines
15 ("sultaines"), C₁₀-C₁₈ amine oxides; and mixtures thereof.

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Polyhydroxy Fatty Acid Amide Surfactant

The detergent compositions hereof may also contain polyhydroxy fatty acid amide surfactant. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein: R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R² is a C₅-C₃₁ hydrocarbyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₅ alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂(CHOR')(CHOH)-CH₂OH, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly -CH₂-(CHOH)₄-CH₂OH.

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxyethyl, or N-2-hydroxy propyl.

R²-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

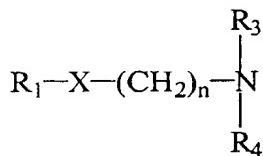
Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to

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form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

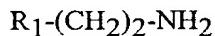
Amine Surfactants

Suitable amine surfactants for use herein include deterotive amines according to the formula:

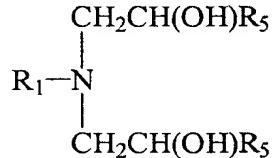


wherein R_1 is a $\text{C}_6\text{-C}_{12}$ alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH , CONH , COO , or O or X can be absent; and R_3 and R_4 are individually selected from H , $\text{C}_1\text{-C}_4$ alkyl, or $(\text{CH}_2\text{-CH}_2\text{-O(R}_5\text{)})$ wherein R_5 is H or methyl.

Preferred amines include the following:



$\text{R}_1\text{-C(O)-NH-(CH}_2)_3\text{-N(CH}_3)_2$



wherein R_1 is a $\text{C}_6\text{-C}_{12}$ alkyl group and R_5 is H or CH_3 .

In a highly preferred embodiment, the amine is described by the formula:



wherein R_1 is $\text{C}_8\text{-C}_{12}$ alkyl.

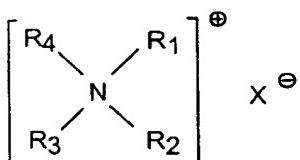
Particularly preferred amines include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, $\text{C}_8\text{-C}_{12}$ bis(hydroxyethyl)amine, $\text{C}_8\text{-C}_{12}$ bis(hydroxyisopropyl)amine, and $\text{C}_8\text{-C}_{12}$ amido-propyl dimethyl amine, and mixtures.

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If utilized the detergents amine comprise from about 0.1% to about 10%, preferably from about 0.5% to about 5%, by weight of the composition.

Quaternary Ammonium Surfactants

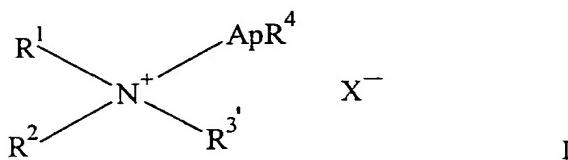
5 From about 1% to about 6% of a quaternary ammonium surfactant having the formula

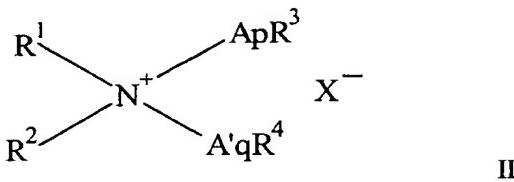


wherein R₁ and R₂ are individually selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl, and -(C₂H₄O)_xH where x has a value from about 2 to about 5; X is an anion; and (1) R₃ and R₄ are each a C₆-C₁₄ alkyl or (2) R₃ is a C₆-C₁₈ alkyl, and R₄ is selected 10 from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ hydroxy alkyl, benzyl, and -(C₂H₄O)_xH where x has a value from 2 to 5;

Preferred quaternary ammonium surfactants are the chloride, bromide, and methylsulfate salts. Examples of preferred mono-long chain alkyl quaternary ammonium surfactants are those wherein R₁, R₂, and R₄ are each methyl and R₃ is a C₈-C₁₆ alkyl; or wherein R₃ is C₈-C₁₈ alkyl 15 and R₁, R₂, and R₄ are selected from methyl and hydroxy-alkyl moieties. Lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxyethylammonium methylsulfate, di-C₁₂-C₁₄ alkyl dimethyl ammonium chloride, and mixtures thereof are particularly preferred. ADOGEN 412TM, a lauryl trimethyl ammonium chloride commercially available from Witco, is also preferred. Even more highly preferred are the lauryl trimethyl ammonium chloride and myristyl trimethyl ammonium chloride.

20 25 Alkoxylated quaternary ammonium (AQA) surfactants useful in the present invention are of the general formula:





wherein R¹ is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, 5 preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R² and R³ are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; R³ and R⁴ can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from C₁-C₄ alkoxy, especially ethoxy (i.e., 10 -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; and for formula I, p is from 2 to about 30, preferably 2 to about 15, most preferably 2 to about 8; and for formula II, p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

Other quaternary surfactants include the ammonium surfactants such as 15 alkyldimethylammonium halogenides, and those surfactants having the formula: [R²(OR³)_y][R⁴(OR³)_y]₂R⁵N⁺X⁻ wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group 20 consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl, ring structures formed by joining the two R⁴ groups, -CH₂CHOHCHOHCOR⁶CHOH-CH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not O; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to 25 about 15; and X is any compatible anion.

*Non-Surfactant Components**Fatty Acids*

For the purposes of calculating the Hydrophilic Index of this invention, fatty acids are not considered a surfactant. Fatty acids are, however, preferred for use in the present compositions. Especially preferred is rapeseed fatty acid. Other suitable fatty acids include saturated and/or unsaturated fatty acids obtained from natural sources or synthetically prepared. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid. The fatty acid is preferably present at from about 2% to about 15% by weight of the composition.

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Electrolytes

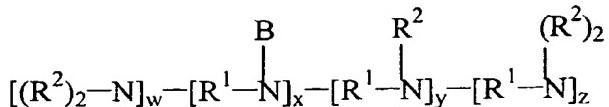
Without being limited by theory, it is believed that the presence of electrolytes acts to control the viscosity of the liquid compositions. Thus, the liquid nature of the compositions herein are affected by the choice of surfactants and by the amount of electrolytes present. In preferred embodiments herein, the compositions will further comprise from 0% to about 10%, more preferably from about 2% to about 6%, even more preferably from about 3% to about 5%, of a suitable electrolyte or acid equivalent thereof. Sodium citrate is a highly preferred electrolyte for use herein.

The compositions herein may optionally contain from about 0% to about 10%, by weight, of solvents and hydrotropes. Without being limited by theory, it is believed that the presence of solvents and hydrotropes can affect the structured versus isotropic nature of the compositions; By "solvent" is meant the commonly used solvents in the detergent industry, including alkyl monoalcohol, di-, and tri-alcohols, ethylene glycol, propylene glycol, propanediol, ethanediol, glycerine, etc. By "hydrotrope" is meant the commonly used hydrotropes in the detergent industry, including short chain surfactants that help solubilize other surfactants. Other examples of hydrotropes include cumene, xylene, or toluene sulfonate, urea, C₈ or shorter chain alkyl carboxylates, and C₈ or shorter chain alkyl sulfate and ethoxylated sulfates.

Modified polyamine

The compositions herein may comprise at least about 0.05%, preferably from about 0.05% to about 3%, by weight, of a water-soluble or dispersible, modified polyamine agent, said agent comprising a polyamine backbone corresponding to the formula:

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wherein each R¹ is independently C₂-C₅ alkylene, alkenylene or arylene; each R² is independently H, or a moiety of formula OH[(CH₂)_xO]_n, wherein x is from about 1 to about 8 and n is from about 10 to about 50; w is 0 or 1; x+y+z is from about 5 to about 30; and B

5 represents a continuation of this structure by branching; and wherein said polyamine before alkylation has an average molecular weight of from about 300 to about 1,200.

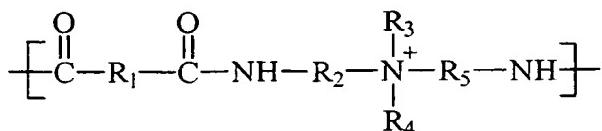
In preferred embodiments, R¹ is C₂-C₄ alkylene, more preferably ethylene; R² is OH[CH₂CH₂O]_n, wherein n is from about 15 to about 30, more preferably n is about 20. The average Molecular Weight of the polyamine before alkylation is from about 300 to about 1200, 10 more preferably from about 500 to about 900, still more preferably from about 600 to about 700, even more preferably from about 600 to about 650.

In another preferred embodiment, R¹ is C₂-C₄ alkylene, more preferably ethylene; R² is OH[CH₂CH₂O]_n, wherein n is from about 10 to about 20, more preferably n is about 15. The average Molecular Weight of the polyamine before alkylation is from about 100 to about 300, 15 more preferably from about 150 to about 250, even more preferably from about 180 to about 200.

Polyamide-Polyamines

The liquid compositions of the present invention preferably comprise from about 0.1% to 8% by the weight of the composition of certain polyamide-polyamines. More preferably, such 20 polyamide-polyamine materials will comprise from about 0.5% to 4% by weight of the compositions herein. Most preferably, these polyamide-polyamines will comprise from about 1% to 3% by weight of the composition.

The polyamide-polyamine materials used in this invention are those which have repeating, substituted amido-amine units which correspond to the general Structural Formula No. I as 25 follows:



Structural Formula No. I

In Structural Formula No. I, R₁, R₂ and R₅ are each independently C₁-4 alkylene, C₁-4 alkarylene or arylene. It is also possible to eliminate R₁ entirely so that the polyamide- 30 polyamine is derived from oxalic acid.

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Also in Structural Formula No. I, R₃ is H, epichlorohydrin, an azetidinium group, an epoxypropyl group or a dimethylaminohydroxypropyl group, and R₄ can be H, C₁₋₄ alkyl, C₁₋₄ alkaryl, or aryl. R₄ may also be any of the foregoing groups condensed with C₁₋₄ alkylene oxide.

5 R₁ is preferably butylene, and R₂ and R₅ are preferably ethylene. R₃ is preferably epichlorohydrin. R₄ is preferably H.

The polyamide-polyamine materials useful herein can be prepared by reacting polyamines such as diethylenetriamine, triethylenetetraamine, tetraethylenepentamine or dipropyleneetriamine with C₂-C₁₂ dicarboxylic acids such as oxalic, succinic, glutaric, adipic and diglycolic acids.

10 Such materials may then be further derivatized by reaction with, for example, epichlorohydrin. Preparation of such materials is described in greater detail in Keim, U.S. Patent 2,296,116, Issued February 23, 1960; Keim, U.S. Patent 2,296,154, Issued February 23, 1960 and Keim, U.S. Patent 3,332,901, Issued July 25, 1967.

The polyamide-polyamine agents preferred for use herein are commercially marketed by
15 Hercules, Inc. under the tradename Kymene® . Especially useful are Kymene 557H® and Kymene 557LX® which are epichlorohydrin adducts of polyamide-polyamines which are the reaction products of diethylenetriamine and adipic acid. Other suitable materials are those marketed by Hercules under the tradenames Reten® and Delsette®, and by Sandoz under the tradename Cartaretin®. These polyamide-polyamine materials are marketed in the form of
20 aqueous suspensions of the polymeric material containing, for example, about 12.5% by weight of solids.

Polyethoxylated-Polyamine Polymers

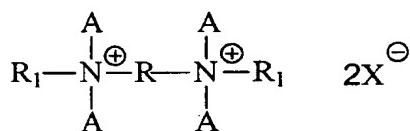
Another polymer dispersant form use herein includes polyethoxylated-polyamine polymers (PPP). The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's). A common polyalkyleneamine (PAA) is tetrabutylpentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and
30 teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See

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U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Polyethoxylated polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951

10 Optionally, but preferred polyethoxylated-polyamine polymers useful for this invention are alkoxylated quaternary diamines of the general formula:



where R is selected from linear or branched C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, [(CH₂CH₂O)_qCH₂CH₂]- and -CH₂CH(OH)CH₂O-(CH₂CH₂O)_qCH₂CH(OH)CH₂]- where q is from about 1 to about 100. Each R₁ is independently selected from C₁-C₄ alkyl, C₇-C₁₂ alkylaryl, or A. A is of the formula:

20 $(\text{CH}-\text{CH}_2-\text{O})_n\text{B}$
 |
 R₃

where R₃ is selected from H or C₁-C₃ alkyl, n is from about 5 to about 100, and B is selected from H, C₁-C₄ alkyl, acetyl, or benzoyl; X is a water soluble anion.

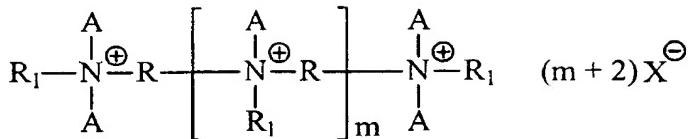
In preferred embodiments, R is selected from C₄ to C₈ alkylene, R₁ is selected from C₁-C₂ alkyl or C₂-C₃ hydroxyalkyl, and A is:

25 $(\text{CH}-\text{CH}_2-\text{O})_n\text{H}$
 |
 R₃

where R₃ is selected from H or methyl, and n is from about 10 to about 50.

30 In another preferred embodiment R is linear or branched C₆, R₁ is methyl, R₃ is H, and n is from about 20 to about 50.

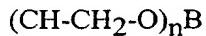
Additional alkoxylated quaternary polyamine dispersants which can be used in the present invention are of the general formula:



where R is selected from linear or branched C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, [(CH₂CH₂O)_qCH₂CH₂]- and -CH₂CH(OH)CH₂O-

5 (CH₂CH₂O)_qCH₂CH(OH)CH₂]- where q is from about 1 to about 100. If present, Each R₁ is independently selected from C₁-C₄ alkyl, C₇-C₁₂ alkylaryl, or A. R₁ may be absent on some nitrogens; however, at least three nitrogens must be quaternized.

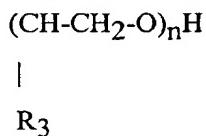
A is of the formula:



10 |
R₃

where R₃ is selected from H or C₁-C₃ alkyl, n is from about 5 to about 100 and B is selected from H, C₁-C₄ alkyl, acetyl, or benzoyl; m is from about 0 to about 4, and X is a water soluble anion.

15 In preferred embodiments, R is selected from C₄ to C₈ alkylene, R₁ is selected from C₁-C₂ alkyl or C₂-C₃ hydroxyalkyl, and A is:



20 where R₃ is selected from H or methyl, and n is from about 10 to about 50; and m is 1.

In another preferred embodiment R is linear or branched C₆, R₁ is methyl, R₃ is H, and n is from about 20 to about 50, and m is 1.

The levels of these polyethoxylated-polyamine polymers used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These polyethoxylated-polyamine polymers can be synthesized following the methods outline in U.S. Patent No. 4,664,848, or other ways known to those skilled in the art.

Enzymes

Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima,

thermostability, and stability to active bleach, detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated into detergent or detergent additive compositions at 5 levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as dishware and the like. "Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent 10 composition.

In practical terms for current commercial preparations, the compositions herein may preferably the enzyme is present in an amount of from about 0.0001% to about 1.5%, more preferably from about 0.00018% to about 1.0%, and most preferably from about 0.00024% to 15 about 0.5%, by weight of the detergent composition of the pure enzyme. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 25 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

i) Mannanase

30 A preferred element of the detergent compositions of the present invention is a mannanase enzyme. Encompassed in the present invention are the following three mannans-degrading enzymes : EC 3.2.1.25 : β -mannosidase, EC 3.2.1.78 : Endo-1,4- β -mannosidase, referred therein after as "mannanase" and EC 3.2.1.100 : 1,4- β -mannobiosidase (IUPAC Classification- Enzyme nomenclature, 1992 ISBN 0-12-227165-3 Academic Press).

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More preferably, the detergent compositions of the present invention comprise a β -1,4-Mannosidase (E.C. 3.2.1.78) referred to as Mannanase. The term "mannanase" or "galactomannanase" denotes a mannanase enzyme defined according to the art as officially being named mannan endo-1,4-beta-mannosidase and having the alternative names beta-mannanase and 5 endo-1,4-mannanase and catalysing the reaction: random hydrolysis of 1,4-beta-D- mannosidic linkages in mannans, galactomannans, glucomannans, and galactoglucomannans.

In particular, Mannanases (EC 3.2.1.78) constitute a group of polysaccharases which degrade mannans and denote enzymes which are capable of cleaving polyose chains containing mannose units, i.e. are capable of cleaving glycosidic bonds in mannans, glucomannans, 10 galactomannans and galactogluco-mannans. Mannans are polysaccharides having a backbone composed of β -1,4- linked mannose; glucomannans are polysaccharides having a backbone or more or less regularly alternating β -1,4 linked mannose and glucose; galactomannans and galactoglucomannans are mannans and glucomannans with α -1,6 linked galactose sidebranches. These compounds may be acetylated.

15 The degradation of galactomannans and galactoglucomannans is facilitated by full or partial removal of the galactose sidebranches. Further the degradation of the acetylated mannans, glucomannans, galactomannans and galactogluco-mannans is facilitated by full or partial deacetylation. Acetyl groups can be removed by alkali or by mannan acetylesterases. The oligomers which are released from the mannanases or by a combination of mannanases and α - 20 galactosidase and/or mannan acetyl esterases can be further degraded to release free maltose by β -mannosidase and/or β -glucosidase.

Mannanases have been identified in several *Bacillus* organisms. For example, Talbot et al., Appl. Environ. Microbiol., Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus* in dimer form having molecular weight of 162 kDa and 25 an optimum pH of 5.5-7.5. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551- 555 (1994) describes a beta-mannanase derived from *Bacillus subtilis* having a molecular weight of 38 kDa, an optimum activity at pH 5.0 and 55C and a pI of 4.8. JP-03047076 discloses a beta-mannanase derived from *Bacillus* sp., having a molecular weight of 373 kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. JP-63056289 describes the production of an 30 alkaline, thermostable beta-mannanase which hydrolyses beta-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno-oligosaccharides. JP-63036774 relates to the *Bacillus* microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase at an alkaline pH. JP-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp. AM-001. A purified mannanase from *Bacillus amyloliquefaciens* useful in the bleaching of pulp and

paper and a method of preparation thereof is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active at an extreme pH and temperature. WO 94/25576 discloses an enzyme from *Aspergillus aculeatus*, CBS 101.43, exhibiting mannanase activity which may be useful for degradation or modification of plant or 5 algae cell wall material. WO 93/24622 discloses a mannanase isolated from *Trichoderma reseei* useful for bleaching lignocellulosic pulps. An hemicellulase capable of degrading mannan-containing hemicellulose is described in WO91/18974 and a purified mannanase from *Bacillus amyloliquefaciens* is described in WO97/11164.

Preferably, the mannanase enzyme will be an alkaline mannanase as defined below, more 10 preferably, a mannanase originating from a bacterial source. Especially, the laundry detergent composition of the present invention will comprise an alkaline mannanase selected from the mannanase from the strain *Bacillus agaradherens* NICMB 40482; the mannanase from *Bacillus subtilis* strain 168, gene yght; the mannanase from *Bacillus sp.* I633 and/or the mannanase from *Bacillus sp.* AAI12. Most preferred mannanase for the inclusion in the detergent compositions of 15 the present invention is the mannanase enzyme originating from *Bacillus sp.* I633 as described in the co-pending application No. PA 1998 01340.

The terms "alkaline mannanase enzyme" is meant to encompass an enzyme having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a given pH ranging from 7 to 12, preferably 7.5 to 10.5.

20 The alkaline mannanase from *Bacillus agaradherens* NICMB 40482 is described in the co-pending U.S. patent application serial No. 09/111,256. More specifically, this mannanase is:

- i) a polypeptide produced by *Bacillus agaradherens*, NCIMB 40482; or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 32-343 of SEQ ID NO:2 as shown in U.S. patent application serial No. 09/111,256; or
- 25 iii) an analogue of the polypeptide defined in i) or ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.
- 30 Also encompassed is the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:
 - (a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from

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nucleotide 97 to nucleotide 1029 as shown in U.S. patent application serial No. 09/111,256;

- (b) species homologs of (a);
- (c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 32 to amino acid residue 343 as shown in U.S. patent application serial No. 09/111,256;
- (d) molecules complementary to (a), (b) or (c); and
- (e) degenerate nucleotide sequences of (a), (b), (c) or (d).

10 The plasmid pSJ1678 comprising the polynucleotide molecule (the DNA sequence) encoding said mannanase has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, 15 Federal Republic of Germany, on 18 May 1998 under the deposition number DSM 12180.

A second more preferred enzyme is the mannanase from the *Bacillus subtilis* strain 168, which is described in the co-pending U.S. patent application serial No. 09/095,163. More specifically, this mannanase is:

- i) is encoded by the coding part of the DNA sequence shown in SED ID No. 5 shown in the U.S. patent application serial No. 09/095,163 or an analogue of said sequence; and/or
- ii) a polypeptide comprising an amino acid sequence as shown SEQ ID NO:6 shown in the U.S. patent application serial No. 09/095,163; or
- iii) an analogue of the polypeptide defined in ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed in the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

- (a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO:5 as shown in the U.S. patent application serial No. 09/095,163
- (b) species homologs of (a);

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- (c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 6 as shown in the U.S. patent application serial No. 09/095,163;
- (d) molecules complementary to (a), (b) or (c); and
- 5 (e) degenerate nucleotide sequences of (a), (b), (c) or (d).

A third more preferred mannanase is described in the co-pending Danish patent application No. PA 1998 01340. More specifically, this mannanase is:

- 10 i) a polypeptide produced by *Bacillus sp.* I633;
- ii) a polypeptide comprising an amino acid sequence as shown in positions 33-340 of SEQ ID NO:2 as shown in the Danish application No. PA 1998 01340; or
- 15 iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of:

- 20 (a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 317 to nucleotide 1243 the Danish application No. PA 1998 01340;
- (b) species homologs of (a);
- (c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 33 to amino acid residue 340 the Danish application No. PA 25 1998 01340;
- (d) molecules complementary to (a), (b) or (c); and
- (e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM3 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the 30 *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 29 May 1998 under the deposition number DSM 12197.

A fourth more preferred mannanase is described in the Danish co-pending patent application No. PA 1998 01341. More specifically, this mannanase is:

- i) a polypeptide produced by *Bacillus sp.* AAI 12;
- ii) a polypeptide comprising an amino acid sequence as shown in positions 25-362 of
5 SEQ ID NO:2as shown in the Danish application No. PA 1998 01341; or
- iii) an analogue of the polypeptide defined in i) or ii) which is at least 65%
homologous with said polypeptide, is derived from said polypeptide by
substitution, deletion or addition of one or several amino acids, or is
immunologically reactive with a polyclonal antibody raised against said
10 polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of

- (a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from
15 nucleotide 225 to nucleotide 1236 as shown in the Danish application No. PA 1998 01341;
- (b) species homologs of (a);
- (c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from
20 amino acid residue 25 to amino acid residue 362 as shown in the Danish application No. PA 1998 01341;
- (d) molecules complementary to (a), (b) or (c); and
- (e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM1 comprising the polynucleotide molecule (the DNA sequence)
25 encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 7 October 1998 under the deposition
30 number DSM 12433.

ii) Amylase Variants

The amylase variants used in the present invention include, but are not limited to, the amylase enzymes described in WO 95/26397 and in WO 96/23873 (Novo). These enzymes are

incorporated into cleaning compositions at a level of from about 0.0001%, preferably from about 0.00018%, more preferably from about 0.00024%, most preferably from about 0.05% to about 0.1%, preferably to about 0.060%, more preferably to about 0.048% by weight of the cleaning compositions of pure enzyme.

5 The amylase variants are preferably selected from the group consisting of α -amylase variants. Suitable α -amylase variants for use in the present invention include, but are not limited to the following α -amylases:

- (i) α -amylase characterized by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a 10 pH value in the range of 8 to 10, measured by Phadebas® α -amylase activity assay; and/or
- (ii) α -amylase according to (i) comprising the amino acid sequence shown in SEQ ID No. 1 or an α -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No. 1; and/or
- 15 (iii) α -amylase according to (i) comprising the amino acid sequence shown in SEQ ID No. 2 or an α -amylase being at least 80% homologous with the amino acid sequence shown in SEQ ID No. 2; and/or
- (iv) α -amylase according to (i) comprising the following amino acid sequence N-terminal: His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-20 Tyr-Leu-Pro-Asn-Asp (SEQ ID No. 3) or an α -amylase being at least 80% homologous with the amino acid sequence shown (SEQ ID No. 3) in the N-terminal; and/or
- (v) α -amylase according to (i-iv) wherein the α -amylase is obtainable from an alkalophilic *Bacillus* species; and/or
- 25 (vi) α -amylase according to (v) wherein the amylase is obtainable from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935; and/or
- (vii) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to SEQ ID No. 1, ID No. 2, or ID No. 3; and/or
- 30 (viii) variant of a parent α -amylase, wherein the parent α -amylase (1) has one of the amino acid sequences shown in SEQ ID No. 1, ID No. 2, or ID No. 4, respectively, or (2) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an

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- antibody raised against an α -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an α -amylase having one of said amino acid sequences, in which variants: (A) at least one amino acid residue of said parent α -amylase has been deleted; and/or (B) at least one amino acid residue of said parent α -amylase has been replaced by a different amino acid residue; and/or (C) at least one amino acid residue has been inserted relative to said parent α -amylase; said variant having an α -amylase activity and exhibiting at least one of the following properties relative to said parent α -amylase: increased thermostability; increased stability towards oxidation; reduced Ca ion dependency; increased stability and/or α -amyloytic activity at neutral to relatively high pH values; increased α -amyloytic activity at relatively high temperature; and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α -amylase variant to the pH of the medium.
- A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%.
- In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a *Bacillus* strain but also an amylase encoded by a DNA sequence isolated from such a *Bacillus* strain and produced in a host organism transformed with the DNA sequence.

iii) Protease

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and

a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is
5 described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in
10 combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US
15 Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303,761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European
20 Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein, Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985.

Also preferred proteases are subtilisin enzymes, in particular BPN', that have been
25 modified by mutating the various nucleotide sequences that code for the enzyme, thereby modifying the amino acid sequence of the enzyme. These modified subtilisin enzymes have decreased adsorption to and increased hydrolysis of an insoluble substrate as compared to the wild-type subtilisin. Also suitable are mutant genes encoding for such BPN' variants.

Preferred BPN' variants comprise wild-type amino acid sequence wherein the wild-type
30 amino acid sequence at one or more of positions 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 218, 219 or 220 is substituted; wherein the BPN'
variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as
compared to the wild-type subtilisin BPN'. Preferably, the positions having a substituted amino

acid are 199, 200, 201, 202, 205, 207, 208, 209, 210, 211, 212, or 215; more preferably, 200, 201, 202, 205 or 207.

Preferred protease enzymes for use according to the present invention also include the subtilisin 309 variants. These protease enzymes include several classes of subtilisin 309 variants.

- 5 A. Loop Region 6 Substitution Variants - These subtilisin 309 variants have a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more of positions 193, 194, 195, 196, 197, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213 or 214; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309. Preferably these proteases have amino acids substituted at 193, 194, 195, 196, 197, 199, 201, 202, 203, 204, 205, 206 or 209; more preferably 194, 195, 196, 199 or 200.
- 10 B. Multi-Loop Regions Substitution Variants - These subtilisin 309 variants may also be a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more positions in one or more of the first, second, third, fourth, or fifth loop regions; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309.
- 15 C. Substitutions at positions other than the loop regions - In addition, one or more substitution of wild-type subtilisin 309 may be made at positions other than positions in the loop regions, for example, at position 74. If the additional substitution to the subtilisin 309 is mad at position 74 alone, the substitution is preferably with Asn, Asp, Glu, Gly, His, Lys, Phe or Pro, preferably His or Asp. However modifications can be made to one or more loop positions as well as position 74, for example residues 97, 99, 101, 102, 105 and 121.
- 20 25

Subtilisin BPN' variants and subtilisin 309 variants are further described in WO 95/29979, WO 95/30010 and WO 95/30011, all of which were published November 9, 1995, all of which are incorporated herein by reference.

30

iv) **Lipase**

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978.

Other suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Further suitable lipases are
5 lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades). Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var.
lipolyticum NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disynth Co., The Netherlands, and lipases ex
Pseudomonas gladioli. LIPOLASE[®] enzyme derived from *Humicola lanuginosa* and
10 commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein.
Lipase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo.
See also WO 9205249 and RD 94359044.

Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Serial No. 08/341,826. (See also patent
15 application WO 92/05249 viz. wherein the native lipase ex *Humicola lanuginosa* aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.) Preferably the *Humicola lanuginosa* strain DSM 4106 is used.

In spite of the large number of publications on lipase enzymes, only the lipase derived from
20 *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for fabric washing products. It is available from Novo Nordisk under the tradename LipolaseTM, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants. As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal
25 efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor.

Lipase enzyme is incorporated into the composition in accordance with the invention at a
30 level of from 50 LU to 8500 LU per liter wash solution. Preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

-30-

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

5 v) **Cellulase**

The laundry detergent compositions according to the present invention may further comprise at least 0.001% by weight, preferably at least about 0.01%, of a cellulase enzyme. However, an effective amount of cellulase enzyme is sufficient for use in the laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of 10 producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. The compositions herein will typically comprise from about 0.05% to about 2%, preferably from about 0.1% to about 1.5% by weight of a commercial enzyme preparation. The cellulase enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 15 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Preferably, the optimum pH of the enzyme-containing composition is between about 7 and about 9.5.

U. S. Patent No. 4,435,307, Barbesgaard et al, issued March 6, 1984, discloses cellulase produced from *Humicola insolens*. Examples of other suitable cellulases include those produced by a strain of *Humicola insolens*, *Humicola grisea* var. *thermoidea*, and cellulases produced by a 20 species of *Bacillus* sp. or *Aeromonas* sp. Other useful cellulases are those extracted from the hepatopancreas of the marine mollusc *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in the following: GB 2,075,028 A (Novo Industri A/S); GB 2,095,275 A (Kao Soap Co., Ltd.); and Horikoshi et al, U.S. Patent No. 3,844,890 (Rikagaku Kenkyusho). In addition, suitable cellulases and methods for their preparation are described in PCT International 25 Publication Number WO 91/17243, published November 14, 1991, by Novo Nordisk A/S.

Cellulases are known in the art and can be obtained from suppliers under the tradenames: Celluzyme®, Endolase®, and Carezyme®.

For industrial production of the cellulases herein it is preferred that recombinant DNA techniques be employed. However other techniques involving adjustments of fermentations or 30 mutation of the microorganisms involved can be employed to ensure overproduction of the desired enzymatic activities. Such methods and techniques are known in the art and may readily be carried out by persons skilled in the art.

vi) **Other Enzymes**

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases 5 such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

Enzyme Stabilizing System

Enzyme-containing, including but not limited to, liquid compositions, herein may 10 comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition. 15 See Severson, U.S. 4,537,706 for a review of Borate stabilizers.

Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), 20 and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired.

25

Perfumes

Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and 30 essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 4%, by weight, of the detergent

compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Material Care Agents

5 The present compositions may optionally contain as corrosion inhibitors and/or anti-tarnish aids one or more material care agents such as silicates. Material care agents include bismuth salts, transition metal salts such as those of manganese, certain types of paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminium fatty acid salts, and mixtures thereof and are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the composition. A
10 preferred paraffin oil is a predominantly branched aliphatic hydrocarbon comprising from about 20 to about 50 carbon atoms with a ratio of cyclic to noncyclic hydrocarbons of about 32 to 68 sold by Wintershall, Salzbergen, Germany as WINOG 70®. Bi(NO₃)₃ may be added. Other corrosion inhibitors are illustrated by benzotriazole, thiols including thionaphthol and thioanthranol, and finely divided aluminium fatty acid salts. All such materials will generally be
15 used judiciously so as to avoid producing spots or films on glassware or compromising the bleaching action of the compositions. For this reason, it may be preferred to formulate without mercaptan anti-tarnishes which are quite strongly bleach-reactive or common fatty carboxylic acids which precipitate with calcium.

20

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.
25

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethyl ethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionate, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.
30

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

5 A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

10 The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

15 *Polymeric Dispersing Agents*

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It 20 is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing 25 suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, 30 ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges

from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 10, 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Other polymeric materials which can be included are polypropylene glycol (PPG), propylene glycol (PG), and polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2)_n\text{CH}_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated

polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

The levels of these dispersants used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These dispersants can be synthesized following the
5 methods outline in US. Patent No. 4,664,848, or other ways known to those skilled in the art.

Dye Fixative Materials

Optionally but preferred for use herein are selected dye fixative materials which do not form precipitates with anionic surfactant.

- 10 The selected dye fixatives useful herein may be in the form of unpolymerized materials, oligomers or polymers. Moreover, the preferred dye fixatives useful herein are cationic. The dye fixative component of the compositions herein will generally comprise from about 0.1% to 5% by the weight of the composition. More preferably, such dye fixative materials will comprise from about 0.5% to 4% by weight of the compositions, most preferably from about 1% to 3%.
15 Such concentrations should be sufficient to provide from about 10 to 100 ppm of the dye fixative in the aqueous washing solutions formed from the laundry detergent compositions herein. More prefearably from about 20 to 60 ppm of the dye fixative will be delivered to the aqueous washing solution, most preferably about 50 ppm.

The non-precipitating dye fixatives useful herein include a number that are commercially
20 marketed by CLARIANT Corporation under the Sandofix® , Sandolec® and Polymer VRN® tradenames. These include, for example, Sandofix SWE®, Sandofix WA®, Sandolec CT®, Sandolec CS®, Sandolec C1®, Sandolec CF®, Sandolec WA® and Polymer VRN® . Other suitable dye fixatives are marketed by Ciba-Geigy Corporation under the tradename Cassofix FRN-300® and by Hoechst Celanese Corporation under the tradename Tinofix EW®.

25

Builders

Detergent builders can optionally but preferably be included in the compositions herein, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal of particulate soils from surfaces. Builder level can vary widely
30 depending upon end use and physical form of the composition. Built detergents typically comprise at least about 1% builder. Liquid formulations typically comprise about 5% to about 50%, more typically 5% to 35% of builder. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional- structure as well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and 5 carbonate minerals other than sodium carbonate or sesquicarbonate; aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid.

10 Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein.

15 P-containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

20 Suitable silicate builders include alkali metal silicates, particularly those liquids and solids having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1, including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL®, e.g., BRITESIL H2O; and layered silicates, e.g., those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043.

25 Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

30 Aluminosilicate builders are especially useful in granular detergents, but can also be incorporated in liquids. Suitable for the present purposes are those having empirical formula: [M_z(AlO₂)_z(SiO₂)_v]·xH₂O wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic

crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP.

Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder

5 polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and Lamberti et al, U.S. 3,635,830, 10 January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Oxydisuccinates are also especially useful in such compositions and combinations.

20 Certain detergents surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as detergents surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C₅-C₂₀ alkyl and alkenyl 25 succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions as surfactant.builder materials alone or in 30 combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 1967. See also Diehl, U.S. 3,723,322.

DE2006905/0,200,263

Other types of inorganic builder materials which can be used have the formula $(M_x)_i Ca_y (CO_3)_z$ wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25, M_i are cations, at least one of which is a water-soluble, and the equation $\Sigma_i = 1 - 15(x_i \text{ multiplied by the valence of } M_i) + 2y = 2z$ is satisfied such that the formula has a neutral or "balanced" charge. These builders are referred to herein as "Mineral Builders".

Polymeric Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. See U.S. 4,711,730, December 8, 1987 to Gosselink et al, for examples of those produced by transesterification/ oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al.

SRA's also include simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; and the C₁-C₄ alkylcelluloses and C₄ hydroxyalkyl cellulosics; see U.S. 4,000,093, December 28, 1976 to

Nicol, et al. Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN 5 SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 90-80% by weight of polyoxyethylene terephthalate, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

10 U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na 2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na-dimethyl 5-sulfoisophthalate, EG and PG.

Additional classes of SRA's include (I) nonionic terephthalates using diisocyanate coupling agents to link up polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 15 4,240,918 Lagasse et al; (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With a proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting 20 materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.; (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both 25 nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF made, by grafting acrylic monomers on to sulfonated polyesters; these SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie; (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate on to proteins such as caseins, see EP 457,205 A to BASF (1991); (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al, DE 2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 30 4,240,918, 4,787,989, 4,525,524 and 4,877,896.

Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to,

5 derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

10 Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the amino-coumarins. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinyl-pyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, 25 piperidine and derivatives thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

The N-O group can be represented by the following general structures:

30 The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most

preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 5 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a poly-vinyl-pyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 10 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 15,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 15 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

20 Particular brightener species, commercially marketed under the tradenames Tinopal-UNPA-GX, Tinopal AMS-GX, and Tinopal 5BM-GX by Ciba-Geigy Corporation, are also included. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

25 *Suds Suppressors*

Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well 30 known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have

hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

- The detergent compositions herein may also contain non-surfactant suds suppressors.
- 5 These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24
10 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form.
Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al.
- 15 Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example,
20 disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

- 25 Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

- Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl
30 alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the

trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

Alkoxylated Polycarboxylates

5 Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula -(CH₂CH₂O)_m(CH₂)_nCH₃ wherein m is 2-3 and n is 6-12. The
10 side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

15 *Fabric Softeners*

Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with
20 fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Method of Using the Composition

25 The compositions of this invention can be used to form aqueous washing solutions for use in the laundering of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered therewith.

30 An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing solution.

EXAMPLES

AE = Alcohol Ethoxylate

APA = Amino Propyl Amine

AS = Alkyl Sulfate

5 #EO = the average number of ethoxylation units per surfactant molecule

FA = Fatty Acid

CMG = N-Cocoyl N-Methyl Glucamine

LAS = Linear Alkyl Benzene Sulfonate

LTAC = Lauryl Trimethyl Ammonium Chloride

10 MEA = Monoethanolamine

Polymer A = tetraethylenepentaamine with an average degree of ethoxylation of 15

RPS = Rapeseed

TMS/TDS = a mixture of tartrate monosuccinate and tartrate disuccinate

S = Sulfate

EXAMPLE I

Table I illustrates how the Hydrophilic Index is calculated for various surfactants that are commonly used in laundry detergents. In the following table "Cn" is the average chain length of the surfactant molecule, and "phobe" represents the molecular weight of the hydrophobic portion of the surfactant molecule. Likewise, "phil" is the molecular weight of the hydrophilic portion of the surfactant molecule. "Total" is the sum of the phobe and the phil, that is, the average molecular weight of the surfactant molecule. "WF phil" is the weight fraction of the philic portion, that is, the molecular weight of the philic portion divided by the total molecular weight. The "HL_S" is the WF phil multiplied by 20. For ionic surfactants the HI_S value is calculated for the surfactant ion only, i.e., the counterion is ignored.

25 TABLE I

Surfactants	#EO	Cn	phobe	phil	total	WF phil	HI _S
Nonionics							
AE 23-3	3	12.5	176	149	325	.459	9.17
AE 23-5	5	12.5	176	237	413	.574	11.48
AE 23-6.5	6.5	12.5	176	303	479	.633	12.65
AE 23-9	9	12.5	176	413	589	.701	14.02
AE 24-7	7	13	183	325	508	.640	12.80
CMG		13	183	238	421	.565	11.31
Anionics (anions)							
C25AS	0	13.5	190	96	286	.336	6.71
C25AE3.0S	3	13.5	190	228	418	.546	10.91

C25AE1.8S	1.8	13.5	190	175.2	365.2	.480	9.59
C11.8LAS	0	11.8	242.2	80	322.2	.248	4.97
C45E1.0S	1	14.5	204	140	344	.407	8.14
C45E2.25S	2.25	14.5	204	195	399	.489	9.77
C45E3.0S	3	14.5	204	228	432	.528	10.56
Cationics (cations)							
C10 APA		10	141	101	242	.417	8.35
C8-10 APA		9	127	101	228	.443	8.86

EXAMPLE II

The following compositions are intended to illustrate the importance of the Hydrophilic

- 5 Index according to the present invention. Compositions A and B in Table II A, are made according to the present invention. Compositions C through J, in Tables II C and II D, are compositions outside the limits of this invention and are presented for comparative purposes only. Compositions A and B have generally superior cleaning benefits when compared to prior compositions that are outside the limits of the present invention.

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TABLE II A

Surfactants	HIS	A	B
Anionics			
C25AE1.8S	9.59	20.5	
C11.8LAS	4.97	6	3
C45E1.0S	8.14		22.5
Nonionics			
AE23-9	14.02	2	3
Cationics			
C10APA	8.35	1.5	1.5
% Total Surfactant		30	30
% of Surf. As LAS		20.00	10.00
HIC		8.90	8.42
Builders			
Citric Acid		2.5	2.5
C12-14FA		5	
C12-18FA			3.5
RPS FA		6.5	5
Total		14	11

TABLE II B

5

Surfactants	HIS	C	D	E	F	G
Anionics						
CI1.8LAS	4.97	7.2	8.43	11	9.86	6.25
C45E2.25S	9.77	10.8	8.43	10.25	13.8	10.27
Nonionics						
AE23-6.5	12.65	6.5	3.37	4.1		8.1
AE23-9	14.02				2.22	
Cationics						
LTAC	5.18	1.2	0.51			
% Total Surfactant		25.7	20.74	25.35	25.88	24.62

% of Surf. As LAS	.28.02	40.65	43.39	38.10	25.39
HIC	8.94	8.17	8.15	8.31	9.50
Builders					
TMS/TDS		3.37	4.1		
Citric Acid	4	3.37	4.1	7.1	4.5
C12-14FA	15	2.95	0.6		
Total	19	9.69	8.8	7.1	7.1

TABLE II C

Surfactants	HIS	H	I	J
Anionics				
C25AS	6.71			14
C25AE1.8S	9.59		20.15	
C25AE2.5S	10.40	19		
C25AE3.0S	10.91			4
Nonionics				
AE23-9	14.02	2	0.63	
AE24-7	12.80			4.5
CMG	11.31	3.5	2.5	4
Cationics				
C10APA	8.35		0.5	
C8-10APA	8.86			1.3
% Total Surfactant		24.5	23.78	27.8
% of Surf. As LAS		0.00	0.00	0.00
HIC		10.83	9.87	9.06
Builders				
Citric Acid		3	3	1
C12-14FA		2	2	
C12-18FA				7.5
RPS FA				3.1
Total		5	5	11.6

Compositions A and B, which were made according to the present invention, included the additional components listed in Table II D.

TABLE II D

Additional Components Compositions R, S and T	Weight %
DTPA	0.50
manganase	0.01
protease	0.88
amylase	0.10
cellulase	0.05
brightener	0.15
polymer A	1.20
ethanol	0.50
1,2-propanediol	4.00
MEA	0.48
NaOH	7.00
Na ₂ SO ₄	1.75
borax	2.50
suds supressor	0.06
perfume	0.50
dve	0.02
water and Minors	bal.